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Effect of triblock copolymer non-ionic surfactants on the rheology of 3 mol% yttria stabilised zirconia nanosuspensions

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Abstract

The effect of three different molecular weights of a triblock copolymer non-ionic surfactant composed of poly(ethylene oxide) and poly(propylene oxide) have been investigated on the zeta potential, stability and rheology of a commercial nanosuspension of 3 mol% yttria stabilised zirconia (3YSZ). Whilst the surfactants showed some evidence of being adsorbed onto the nanoparticle surfaces, it was in insufficient quantities to achieve complete coverage and measurement of the total organic carbon content suggested that the bulk of the surfactants remained in the liquid medium. As a result, there was only a small effect on the zeta potential. Nevertheless, the stability of the suspension was not affected up to solids contents as high as 54 wt%. Whilst the viscosity of the nanosuspension increased slightly with increasing surfactant concentration due to the presence of the polymer molecules, for the lowest molecular weight surfactant the effect was relatively small. Finally, it was observed that if the ionic strength of the suspension was reduced via the removal of free electrolytes in the suspension by dialysis, the viscosity decreased significantly. The reverse behaviour was also observed when extra NH_4Cl electrolyte was added to the nanosuspension.

Keywords: Nanosuspension; Interparticle interactions; Surfactant; Viscosity

1. Introduction

Nanostructured ceramic materials have received widespread attention in recent years. Their appeal is attributed to their potential to display unusual physical and mechanical properties [1,2]. However, to take advantage of these, the consolidation of the nanoparticles into fully dense and homogeneous engineering parts is required. If this can be achieved without losing the nanoscale features, there is the possibility to use the materials for a very wide range of structural, magnetic, electric or electronic applications [3–5]. To date, dry forming techniques, such as die and isostatic pressing, have not led to defect-free, uniform, high green density components since the resistance of nanopowders to flow is too high due to their very high surface areas, and hence strong adhesive forces between the particles, and the presence of strong agglomerates. As a result it is neither easy to fill the die nor to compact the powder uniformly [6,7].

Colloidal processing, however, offers the potential to modify the surface chemistry of the particles in suspension to encourage them to arrange themselves in orderly, packing-efficient configurations [8–10]. This allows an array of green forming routes to be used, including slip casting, coagulation casting, tape casting and screen printing amongst others [11–13]. However, the first requirement is for stable suspensions with a high solid content, low viscosity and desirable rheological properties.

A great deal of work has been done on the processing of concentrated suspensions of submicron zirconia particles [14–17]. Ionic surfactants such as polyacrylic acid (PAA) and polymethacrylic acid (PMAA) are commonly used electrosteric dispersants, however they are only effective with alkaline suspensions of pH around 9–10, whilst zirconia nanosuspenions tend to be acidic in nature due to the synthesis routes used. In addition, when the particles in a suspension approach ~2 nm from each other the interactions result in a significant increase in viscosity [18], so the finer the particles, the lower the volume fraction at which this occurs. Hence nanosuspensions

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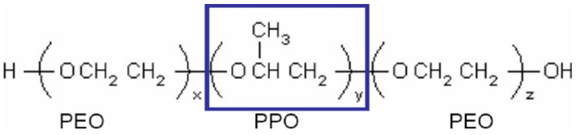
tend to exhibit very high viscosities even at solids contents as low as 20–30 wt%. This results in low green densities in bodies made from the suspensions, which in turn reduces significantly the ability to retain a final grain size of <100 nm during sintering.

In the present work, 3 mol% yttria partially stabilised zirconia (3YSZ) nanoparticles were supplied commercially in the form of a charge stabilised suspension with a pH of ~5. Since industry-standard surfactants such as PAA and PMAA cause flocculation rather than dispersion at this pH, three non-ionic triblock copolymer surfactants of different molecular weight were investigated.

2. Experimental

2.1. Materials

The 3YSZ particles were supplied as a 19.32 wt% solids content colloidal suspension by Nyacol Nano Technologies, Inc., USA; the average particle size was ~100 nm and the pH was 5. Concentration of the suspension was accomplished via evaporation by warming it in a beaker in a hot water bath at a constant temperature of 36 °C with simultaneous stirring using a magnetic stirring system. Three commercial non-ionic surfactants were investigated, viz. L44, F68 and F108, which are part of the range tradenamed Pluronic® (BASF Inc., Germany). They were all triblock copolymers of PEO–PPO–PEO with average molecular weights of 2200, 8400 and 14,600, respectively. The structure, which consists of a hydrophobic backbone with a hydrophilic group attached, may be represented as:



$$H\underbrace{\left(OCH_2\,CH_2\right)_x}_{PEO}\underbrace{\boxed{\left(O\overset{\overset{CH_3}{|}}{C}H\,CH_2\right)_y}}_{PPO}\underbrace{\left(OCH_2\,CH_2\right)_z}_{PEO}OH$$

The ethylene oxide unit on both ends was water soluble whilst the propylene oxide in the middle was not; their combination in single-polymer chains yields a surfactant with amphiphilic characteristics, these are regarded as the best steric stabilisers [19]. The surfactants were dissolved in deionised water to make 10 wt% stock solutions for subsequent use. Ammonium chloride (Fisher Scientific, UK) was used to alter the electrolyte strength of the suspension. The salt crystals were dissolved in deionised water to prepare a 1.0 M NH_4Cl stock solution.

2.2. Zeta potential and agglomerate size measurements

Zeta potential was measured using an electroacoustic technique (AcoustoSizer, Matec Applied Sciences, USA) and 5 wt% solids content suspensions. The latter were prepared by mixing different levels of each surfactant to the as-received 3YSZ nanosuspension and then diluting them using deionised water 24 h later after the surfactants had chance to adsorb onto the particles. The levels of surfactants used ranged from 0 to 30 mg of surfactant per gram of solids present in the suspension. For the zeta potential measurements the pH of the suspensions was initially increased from the as-received value of 5 to ~13 using 1.0 M NaOH and then reduced again to ~5 using 1.0 M HCl, changes in both directions being in pH increments of 1.0.

The agglomerate size distribution of the nanoparticles in the suspensions was monitored using laser diffraction (MasterSizer 2000, Malvern Instruments Ltd., UK). For these measurements, a few drops of each suspension were introduced to a container filled with deionised water to create a very dilute suspension and at least five measurements performed to check reproducibility; in all cases the values observed displayed a negligible standard deviation.

2.3. Viscosity and surface tension measurements

The rheological properties of the suspensions were determined using a rotary viscometer (Bohlin Visco 88 BV, UK) fitted with a concentric cylinder geometry measurement system. About 10 ml of sample was used for each experiment, their temperature being maintained at 20 °C using a water bath attachment. The samples were left to equilibrate for 60 s after being placed in the rheometer and were then exposed to a constant shear rate of 100 s^{-1} for 300 s. The apparent viscosity was calculated as the ratio between the shear stress and the shear rate at 100 s^{-1}.

The surface tension of the suspensions containing varying amounts of F108 and L44, respectively, were measured using a Data Physics OCA20 contact angle measuring system (Carl Stuart UK Ltd., UK). This fully automatic system measures contact angles from images captured during the pendant drop method and yields calculated values of the surface free energies of liquids.

2.4. Adsorption isotherms

Adsorption isotherm measurements were carried out using a total organic carbon (TOC) analyser (Phoenix 8000, Tekmar-Dohrmann, USA), which provided a quantitative analysis of the non-adsorbed fraction of PEO–PPO–PEO in solution. The as-received nanosuspensions were mixed with varying concentrations of the surfactants for 24 h and then ultra-centrifuged at 12,000 rpm for 20 min to separate the solids and liquid medium. The supernatant was immediately decanted and diluted with deionised water for the TOC measurement.

2.5. Dialysis of the suspensions

To determine the critical electrolyte content for the as-received suspension, it was processed in a dialysis kit, Fig. 1, to remove free nitrate and other ions that may have been added during the preparation of the suspension by the manufacturer.

The equipment was based on a Millipore Amicon filter cell that had one end covered with a semi-permeable membrane connected to a pressurised reservoir containing deionised water. The latter was driven into the filter cell where it was mixed with the suspension by a magnetic stirrer. The water then washed the ions through the membrane whilst the nanoparticles were

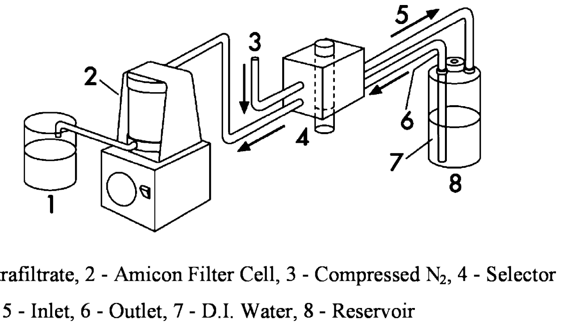


Fig. 1. A schematic of the dialysis equipment for the as-received suspension.

retained in the suspension. After 6 l of water had been used the process was terminated; measurements indicated that the conductivity of the suspension was reduced from 1324 to 260 mS cm^{-1}, indicating the removal of a large amount of ions in the suspension. The product was concentrated to 50 wt% and the viscosity measured with and without surfactant L44 as indicated above.

3. Results and discussion

3.1. Electrokinetic behaviour

Fig. 2 shows the zeta potential measurements of the nanosuspensions with and without the nonionic surfactant F108 present. The positive nature of the zeta potential may be immediately observed; it was this that prevented the commonly used surfactants of polyacrylic acid (PAA) and polymethacrylic acid (PMAA) being used—they result in flocculation of the suspension [20,21] and hence prevent the direct production of homogeneous and dense green bodies. It can also be seen that adding the surfactant had relatively little effect, only decreasing the zeta potential by a small amount due to its adsorption onto the particle surfaces. Finally, it can be observed why the suspension was supplied at a pH of 5; this yields the maximum value for the zeta potential and hence the most dispersed suspension.

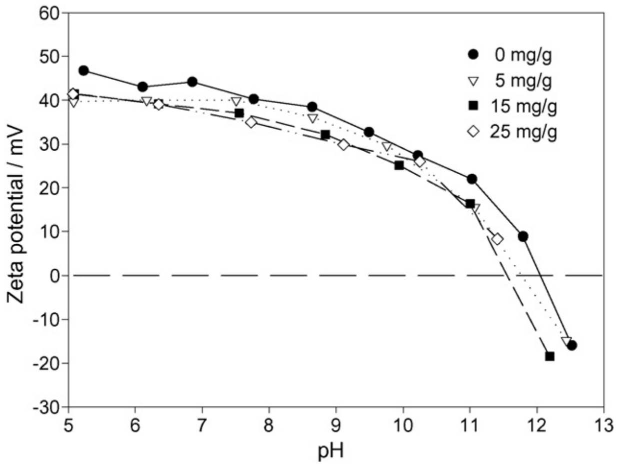


Fig. 2. Zeta potentials of the nanosuspension as a function of pH with differing concentrations of F108.

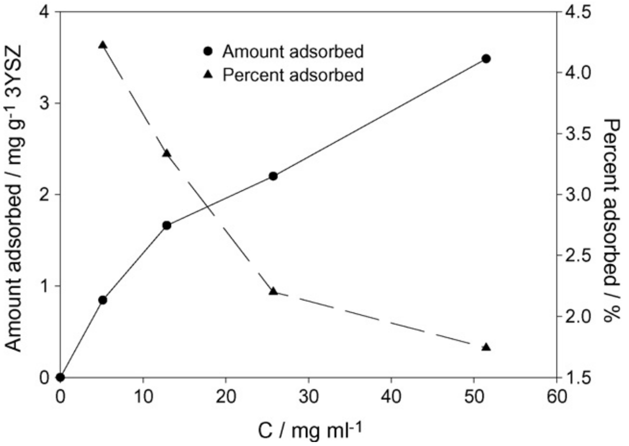


Fig. 3. Adsorption behaviour of F108 on nano-3YSZ in aqueous suspension at pH 5.

3.2. Adsorption of PEO–PPO–PEO onto the nanoparticles

The adsorption isotherms for the F108 and L44 surfactants are shown in Figs. 3 and 4. In both cases it can be seen that whilst the amount of both surfactants absorbed on the nanoparticles increased with increasing surfactant concentration, there was no evidence of complete coverage since a plateau was not reached in the curve. Nevertheless, approximately three times as much of the smaller molecular weight L44 was absorbed compared to the F108; this was not surprising given the difference in the molecular weights of the two surfactants.

3.3. Stability of the nanosuspensions

Despite the failure to achieve complete coverage of the nanoparticles by the surfactants, or to significantly affect the value of the zeta potential by their presence, nevertheless, the suspensions remained dispersed even when concentrated to 54 wt% solids content with increasing F108 content, as shown by the average particle size, d_{50}, in the suspensions, Table 1.

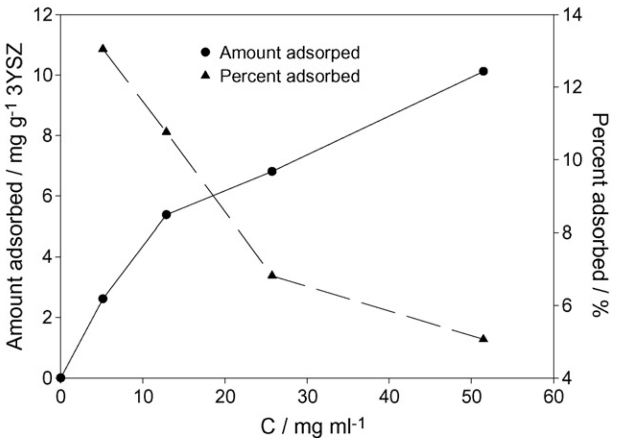


Fig. 4. Adsorption behaviour of L44 on nano-3YSZ in aqueous suspension at pH 5.

Table 1
Stability of 3YSZ + F108 system at a solid content of 54 wt% and pH 5

Concentration of F108 (mg g^{-1})	0	5	10	15	20	30
Particle size, d_{50} (nm)	116	118	117	119	116	118

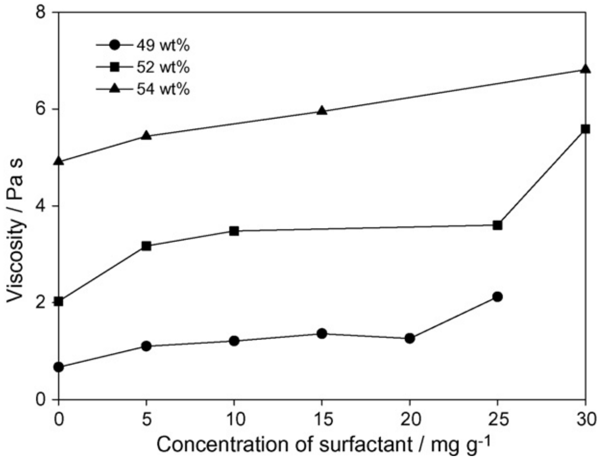


Fig. 5. Viscosity of the nanosuspension as a function of surfactant concentration of F108 for varying solid contents without additional electrolyte NH_4Cl.

3.4. Rheology of the concentrated nanosuspensions

The viscosity of the nanosuspension as a function of surfactant concentration of F108 and solid contents between 49 and 54 wt% is shown in Fig. 5. It can be seen that as both the solids content and the concentration of the surfactant increased so did the viscosity. Regarding the latter, given that Table 1 demonstrated that flocculation did not occur, it is reasonable to suppose that the increase in viscosity was caused by the presence of the surfactant macromolecules in the liquid phase.

Fig. 6 shows that the same effect was observed with all of the molecular weights of surfactant investigated, though, as expected, the lower the molecular weight the smaller the increase in viscosity.

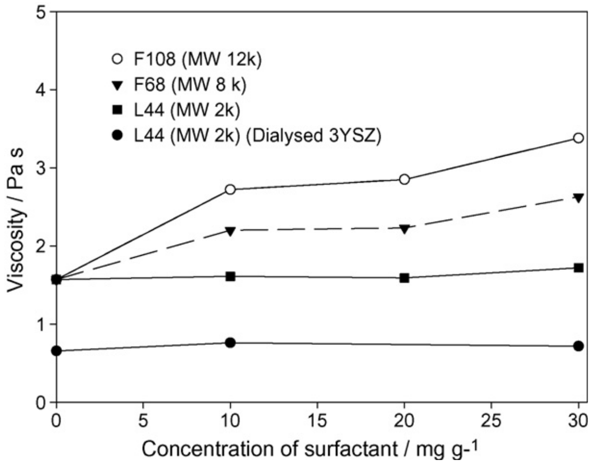


Fig. 6. Viscosity of 50 wt% nanosuspensions as a function of surfactant concentration for different molecular weights.

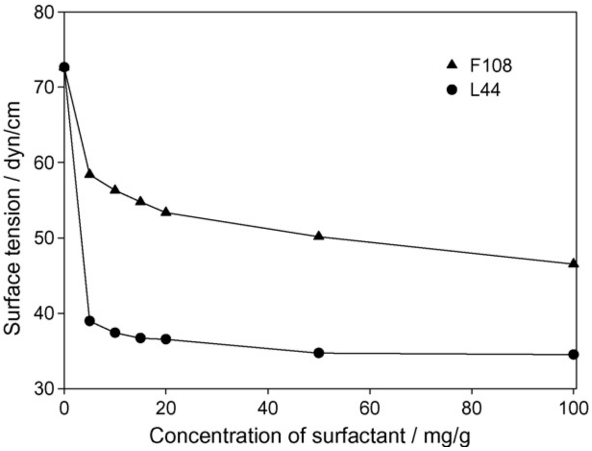


Fig. 7. Surface tension of the nanosuspension with two different surfactants as a function of surfactant concentration.

3.5. Effect of electrolyte strength on rheology of suspensions

When the as-received nanosuspension underwent dialysis to remove the nitrate and other ions present from the manufacture of the suspension the viscosity was observed to decrease significantly, Fig. 6. This is believed to be explained by the minimisation of the electrostatic interactions between the particles [22,23] via the removal of the excess electrolyte in the suspension [24], i.e. the ionic strength of the suspension was reduced. To investigate this further, the ionic strength of the suspension was also increased by the addition of NH_4Cl in the presence of the surfactant L44 and the viscosity measured. However, for the results to be valid the surfactant concentration in the suspension should be constant. This was determined using the method proposed by Saunder [25] in which surfactant was added until the surface tension dropped to the level characteristic of surface saturation. The results are shown in Fig. 7, which indicates that 20 mg g^{-1} of L44 was sufficient to achieve a constant value for the surface tension.

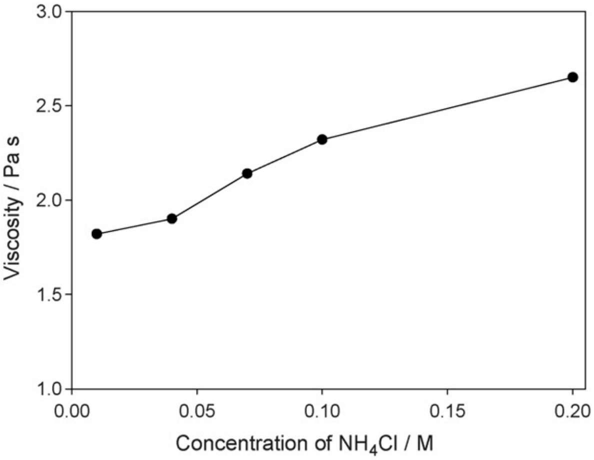


Fig. 8. Viscosity variation at a shear rate of 100 s^{-1} as a function of NH_4Cl concentration in 50 wt% nanosuspension containing 20 mg g^{-1} of L44 at pH 5.

The consequences on the viscosity of increasing the NH_4Cl electrolyte concentration from 0.01 to 0.2 M may be seen in Fig. 8. As expected, the decrease in the electrostatic forces due to the double layer screening effect caused by the addition of the electrolyte resulted in the suspension becoming more viscous.

4. Conclusions

The effect of three different molecular weights of triblock copolymer PEO–PPO–PEO has been studied on the stability of an aqueous nanosuspension of 3YSZ. The results indicate that all three are adsorbed onto the surface of the nanoparticles, but not in sufficient quantity to achieve complete surface coverage even at concentrations as high as 50 mg ml^{-1} of suspension. Nevertheless, the stability of the nanosuspension was maintained to a solid content of 54 wt%. In terms of the rheology of the nanosuspension, the viscosity increased with increasing surfactant content and molecular weight. However the effect was minimal, across the concentration range studied, for the lowest molecular surfactant used, L44, which has a molecular weight of 2200. The viscosity of the nanosuspension could be decreased significantly, however, by decreasing the ionic strength of the suspension via removal of electrolyte ions by dialysis. The reverse effect was observed when electrolyte was added to the suspension.

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